An Exact Value for Avogadro's Number Redux Redux

with comments about the mole and the mass standard

In an article titled *An Exact Value for Avogadro's Number Redux* that I wrote June 17, 2010, I used what was then the most recent NIST value for Avogadro's number (N_A), $6.02214179(30) \times 10^{23}$. Very recently, a new value for Avogadro's number has been published, based on the silicon sphere method using highly enriched silicon (Si). The isotope ^{28}Si is enriched to 99.985% in these samples, as compared with a natural abundance of only 92.23%. The new value for Avogadro's number is reported to be $6.02214129(27) \times 10^{23}$.

In an American Scientist article, it was observed that the crystal structure for both carbon (as diamond) and silicon is a face centered cubic lattice (with 4 atoms per unit cell) modified to contain an extra 4 interior tetrahedrally coordinated atoms per unit cell (a total of 8 atoms per unit cell). If these crystals had been simple cubic lattices then the number of atoms on a edge, n, would have satisfied

$$n^3 = N_A.$$

For an earlier value of Avogadro's number this yielded

$$n = 84{,}446{,}889$$

This is a large number but not incomprehensible like Avogadro's number itself. The last digit is a bit uncertain given the error range quoted for N_A. Instead, for the modified face centered cubic lattice the number of atoms on an edge, k, satisfies the equation

$$8k^3 - 18k^2 + 15k - 4 = N_A$$

In the American Scientist paper, we used the then current value for Avogadro's number, $6.0221415(10) \times 10^{23}$ and got

$$k = 42223444.$$

In the *Redux* paper we had to change this to

$$k = 42223446$$

because Avogadro’s number had changed. However, with the new new value for N_A quoted above, with its 3-fold greater precision, we are back to the k value

$$k = 42223444$$

with the last digit much more certain. Thus the present value of Avogadro’s number and its uncertainty are sufficient to uniquely determine in essence its cube root, the number of atoms on the edge of a real physical structure.

Putting this value into the cubic equation above yields an exact value for N_A given by

$$N_A = 602214108979663699470280$$

That is well within the one standard deviation error range quoted above. Initially N_A was known and k was computed. Since k came out exact *because it must be an integer*, it can be used to determine N_A to all digits. Thus we are not caught in a spurious circle of reasoning.

Avogadro’s number plays a key role in the concept of the mole and for setting a mass standard. In 1971 the definition of the *mole*, an SI base unit, not *el topo*, was given by the CGPM (Conférence Générale des Poids et Mesures) as:

1. The mole is the amount of substance of a system which contains as many elementary entities as there are atoms in 0.012 kilograms of carbon 12; its symbol is “mol.”
2. When the mole is used, the elementary entities must be specified and may be atoms, molecules, ions, electrons, other particles, or specified groups of particles.

These statements need clarification. By carbon 12, one refers to the carbon 12 *nuclide*, exactly 6 protons, 6 neutrons and 6 electrons bound together as an atom. This is electrically neutral but has 4 unpaired electrons and is quite reactive, hardly appropriate for an *elementary* *entity*. It is worth noting that the masses of a free proton and of a free neutron are

$$m_p = 938.272046(21) MeV/c^2$$

$$m_n = 939.565379(21) MeV/c^2$$

while the mass of a free electron is

$$m_e = 0.510998928(11) MeV/c^2$$

Note that the NIST nucleon mass difference is bigger than the electron mass

$$\Delta m_N \equiv m_n - m_p = 1.29333217(42) MeV/c^2$$

The nucleon binding energy for a ^{12}C nucleus is about $7.7\ MeV$ per nucleon, corresponding to a mass defect (or decrease) of $7.7\ MeV/c^2$, an amount greater than the nucleon mass difference and greater than the electron mass. Finally, the binding energy of the 6 electrons in the ^{12}C nuclide is so small that the associated mass reduction compared to the total mass of the atom is only one part in 10 million. All of this means that choosing ^{12}C as a standard for mass uses a highly complex assemblage of particles and is not simply the sum of the parts, so to speak. There is a big difference between having Avogadro's number of ^{12}C atoms and having a face centered crystal made of them. What are we to visualize in the former case, a box of highly reactive atoms in which we somehow keep them apart and have to count them from 1 to N_A. In the latter case we need only guarantee 42,223,444 atoms on an edge of a diamond. This number may well become manageable experimentally and it is comprehensible.

There is now the issue of how much mass is associated with the chemical bonds that hold the diamond together, or that hold the corresponding silicon cube together. Each atom makes 4 tetrahedral bonds with 4 other atoms, or 4 half bonds for a net of 2. A C-C bond in diamond has a bond energy of about 83 kcal/mol and a Si-Si bond has a bond energy of about 42.2 kcal/mol. Converting units and expressing the result for a single bond yields a correction to the mass around one part in a billion. This is ignorable given that it would barely affect only the last digit in 42,223,444. Thus, an exact value for Avogadro's number

$$602214108979663699470280$$

can be used to connect the microscopic mass quantity, one dalton, or one twelfth the mass of a ^{12}C nuclide, with the macroscopic mass quantity, 0.012 kg of a cubic crystal (modified face centered cubic) of enriched ^{12}C having 42,223,444 atoms on each edge. Achieving the pure isotopic ^{12}C crystal will be difficult and such purity may be better done with enriched silicon. The mass standard becomes

$$1\ gram = 602{,}214{,}108{,}979{,}663{,}699{,}470{,}280\ daltons$$

Ronald F. Fox
Smyrna, Georgia
January 14, 2012

PS: One may ask how important it is that the samples, i.e.standards, are at a non-zero temperature such as room temperature. The heat content has mass equivalent to its energy, $m = \frac{E}{c^2}$. Each degree of freedom has an energy content of $\frac{k_B T}{2}$ in which T is the temperature and k_B is Boltzmann's constant. At room temperature, this amounts to $\frac{1}{80}$ eV $=$ 0.0125 eV per degree of freedom. Compared with a nucleon mass, given above, the mass equivalent of the thermal energy is 11 orders of magnitude smaller, and justly ignored.